

Introduction

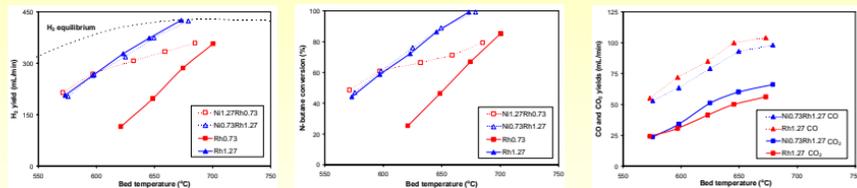
For cost reasons, Ni catalysts used in the industrial production of H₂ are preferred over precious metal catalysts (Rh, Pt, Pd) for reforming natural gas or liquefied petroleum gas (LPG) in integrated fuel processing-fuel cell systems, although precious metal catalysts are more stable than Ni catalysts. Nickel catalysts deactivate due to excessive carbon buildup and the formation of inactive oxidized Ni during shutdown, startup, and turndown cycling.

The objective of this research was to:

- (1) investigate the effect of adding small amounts of a precious metal, Rh, to Ni for suppressing carbon deposition and promoting the reduction of Ni, and
- (2) determine if reducible supports, such as Ce_{0.42}Zr_{0.58}O₂ or CeMgO₃, are better at promoting gasification of carbon than refractory supports, such as La-Al₂O₃.

Reforming Studies

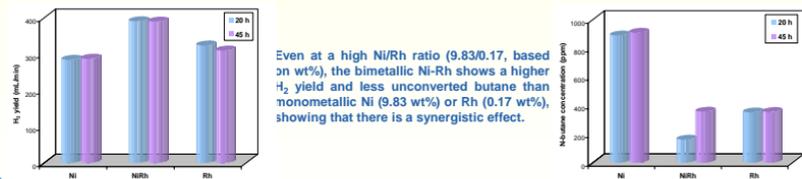
Low total metal Ni+Rh (2 wt%/La-Al₂O₃)



At the higher Rh loading (1.27 wt%), the H₂ yield and butane conversion exhibited by Ni-Rh and Rh are similar. At the lower Rh loading (0.73 wt%), the H₂ yield and butane conversion by Ni-Rh is higher than that by Rh alone.

Because Ni is more active than Rh for the water-gas shift reaction (Wheeler et al., J. Catal. 223 (2004), 191), bimetallic Ni-Rh exhibits a higher CO₂ and lower CO yield than monometallic Rh.

High total metal Ni+Rh (10 wt%/CeZrO₂)



Even at a high Ni/Rh ratio (9.83/0.17, based on wt%), the bimetallic Ni-Rh shows a higher H₂ yield and less unconverted butane than monometallic Ni (9.83 wt%) or Rh (0.17 wt%), showing that there is a synergistic effect.

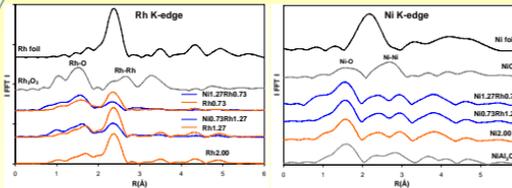
Experimental

- Bimetallic Ni-Rh and monometallic Ni and Rh catalysts were prepared with different Ni/Rh ratios at a total Ni + Rh loading of 2 or 10 wt%. The same weight loadings were used for the Ni and Rh monometallic catalysts.
- Three different supports were investigated: La-Al₂O₃, Ce_{0.42}Zr_{0.58}O₂, and CeMgO₃.
- The Ni-Rh, Ni, and Rh catalysts were evaluated for steam-reforming of *n*-butane (surrogate for LPG) in a microreactor at a steam-to-carbon ratio of 3 and a gas-hourly space velocity of ~50,000 h⁻¹.
- Samples of the fresh and used catalysts were examined using scanning electron microscopy (SEM) for carbon deposits on the catalyst surface, and X-ray absorption spectroscopy (XAS) extended X-ray absorption fine structure analysis (EXAFS) to determine the oxidation and the coordination environment of Ni and Rh.

Conclusions

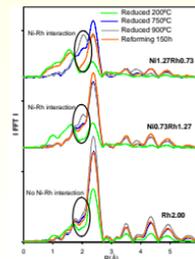
- At Rh weight loadings below 1 wt%, the bimetallic Ni-Rh catalysts exhibited higher H₂ yields and higher butane conversions, compared with monometallic Ni and Rh catalysts at similar weight loadings. At Rh weight loadings above 1 wt%, there was essentially no difference between the H₂ yield and butane conversion exhibited by the bimetallic Ni-Rh and monometallic Rh catalysts.
- In an oxidizing environment, Ni appears to increase the Rh dispersion and stabilize oxidized Rh. Ni is highly oxidized, whether or not Rh is present. Rh does not appear to improve the reducibility of Ni. Under reducing conditions, there is evidence for a Ni-Rh interaction.
- Ni-Rh supported on Ce_{0.42}Zr_{0.58}O₂ exhibited higher H₂ yield and butane conversion than Ni-Rh supported on either La-Al₂O₃ or CeMgO₃. The lack of carbon whiskers on Ni-Rh/Ce_{0.42}Zr_{0.58}O₂ suggests that it can retard carbon deposition by gasifying carbon.

XAS Studies

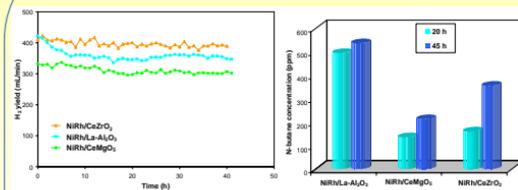


In an oxidizing environment, the contribution of the Rh-Rh shell decreases while that of the Rh-O shell increases as the Ni/Rh ratio increases, suggesting that Ni improves the dispersion of Rh and/or stabilizes oxidized Rh. The similarity in the intensities of the Ni-O and Ni-Ni shells in Ni-Rh and Ni suggests that the coordination environment of Ni is essentially the same and that it is not affected by Rh. A highly oxidized and hard-to-reduce Ni phase, such as NiAl₂O₄ spinel, is observed for all samples.

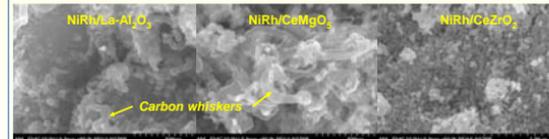
In a reducing environment, a new peak at a radial coordinate of ~2Å is seen for Ni-Rh that is not observed for Rh. Nagaoka and co-workers (J. Catal. 229 (2005), 185) have attributed this peak to Ni-Rh interaction. The intensity of this peak increases as the reduction temperature increases.



Support Effects



Ni-Rh/CeZrO₂ exhibited a higher H₂ yield and less unconverted butane than Ni-Rh/CeMgO₃ or Ni-Rh/La-Al₂O₃. Although the H₂ yields of all three catalysts appeared stable over 45 h, the concentration of unconverted butane increased, suggesting that all catalysts were slowly deactivating. The relative increase in the concentration of unconverted butane was greatest for Ni-Rh/CeZrO₂.



Carbon whiskers were observed with La-Al₂O₃ and CeMgO₃, suggesting that carbon is forming on and diffusing through Ni to the support. The lack of carbon whiskers on CeZrO₂ suggests that it is better able to gasify carbon than La-Al₂O₃ and CeMgO₃.